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# (12) UK Patent Application (19) GB (11) 2 328 684 (13) A

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EP 0712173 A EP 0413313 A WO 96/12676 A

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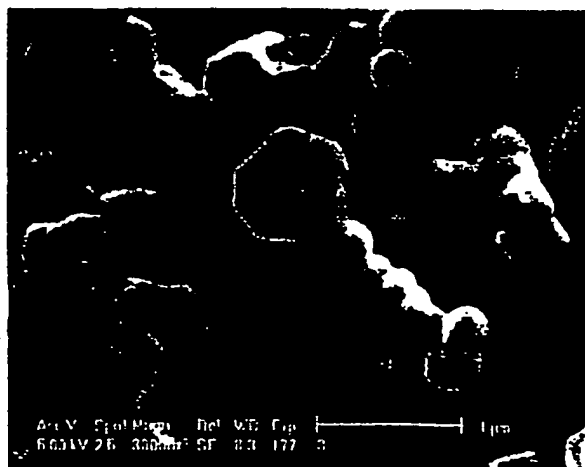
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(54) Abstract Title

A lithium manganese oxide powder and preparation thereof

(57) A lithium manganese oxide ( $\text{Li}_x\text{Mn}_2\text{O}_4$ , where x is 1~1.05) powder has an octahedrol particle shape, and preferably has a particle size of 0.3 - 1 micron and is used as a positive electrode in a lithium secondary battery. In the preparation method lithium acetate and manganese acetate are dissolved in a solvent, gelatine is added to the obtained solution, and the solvent is removed to form a gel. A lithium manganese oxide powder is then formed by calcinating the gel at 300 ~ 500°C, and the powder is ground and sintered at 750 ~ 850°C for 6 ~ 12 hours. The lithium secondary battery adopting a positive electrode containing the lithium manganese oxide as an active material has an improved capacity characteristic and a high-rate changing/discharging characteristic.

FIG. 3



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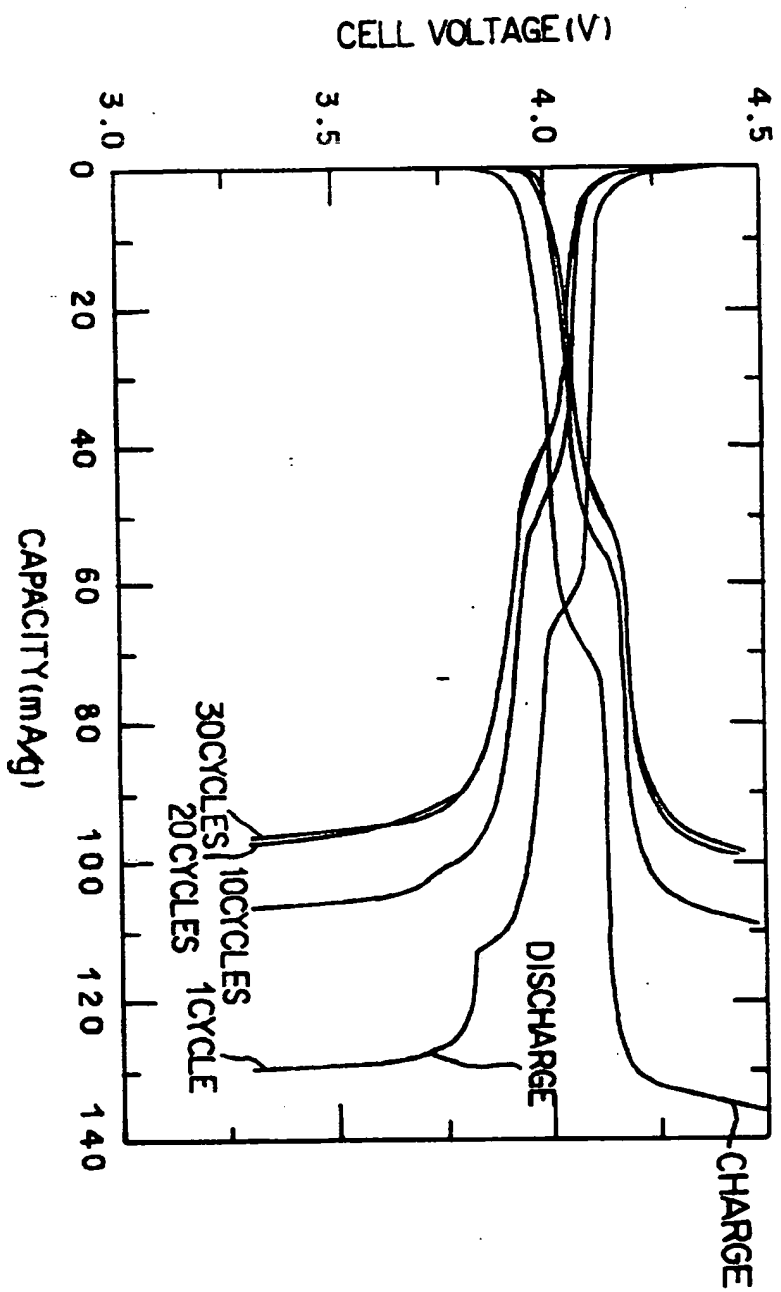


FIG. 1

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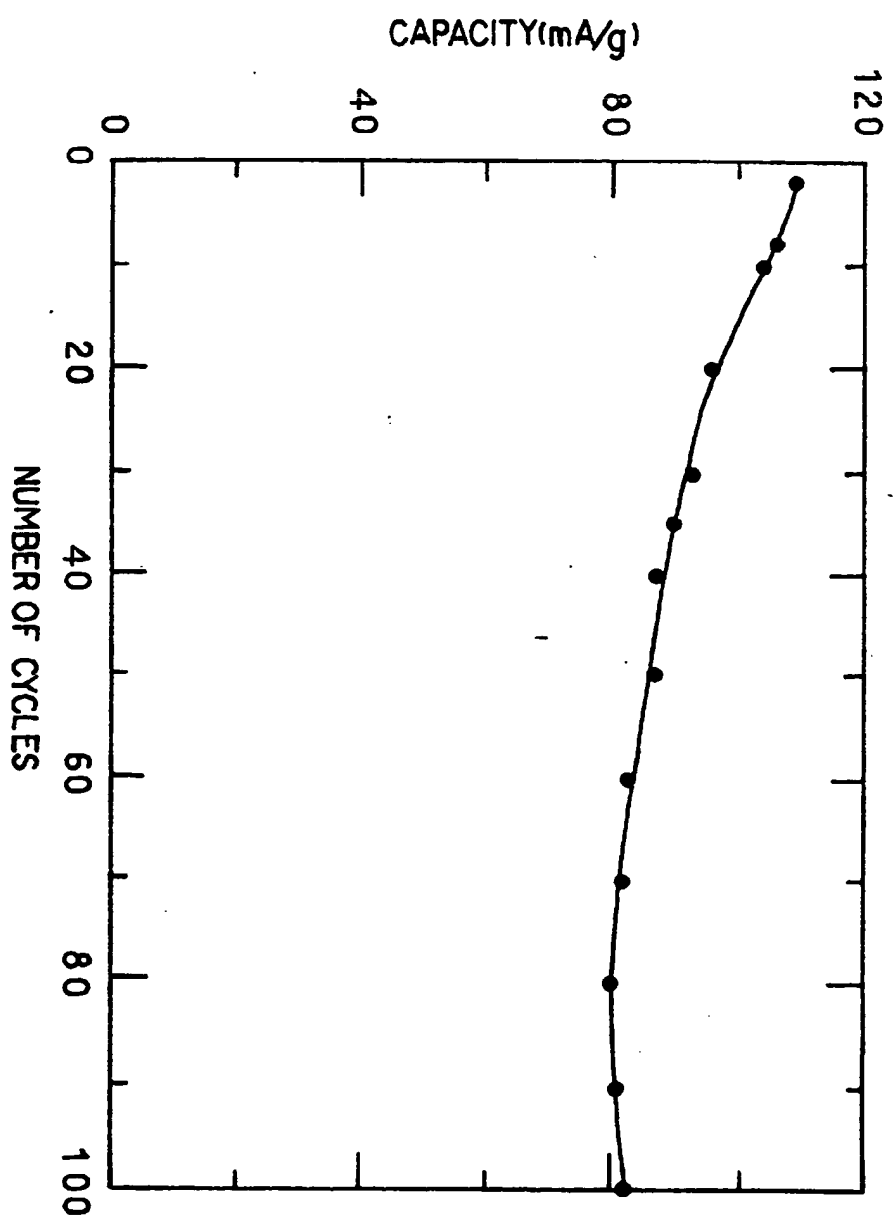


FIG. 2

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FIG. 3



FIG. 4

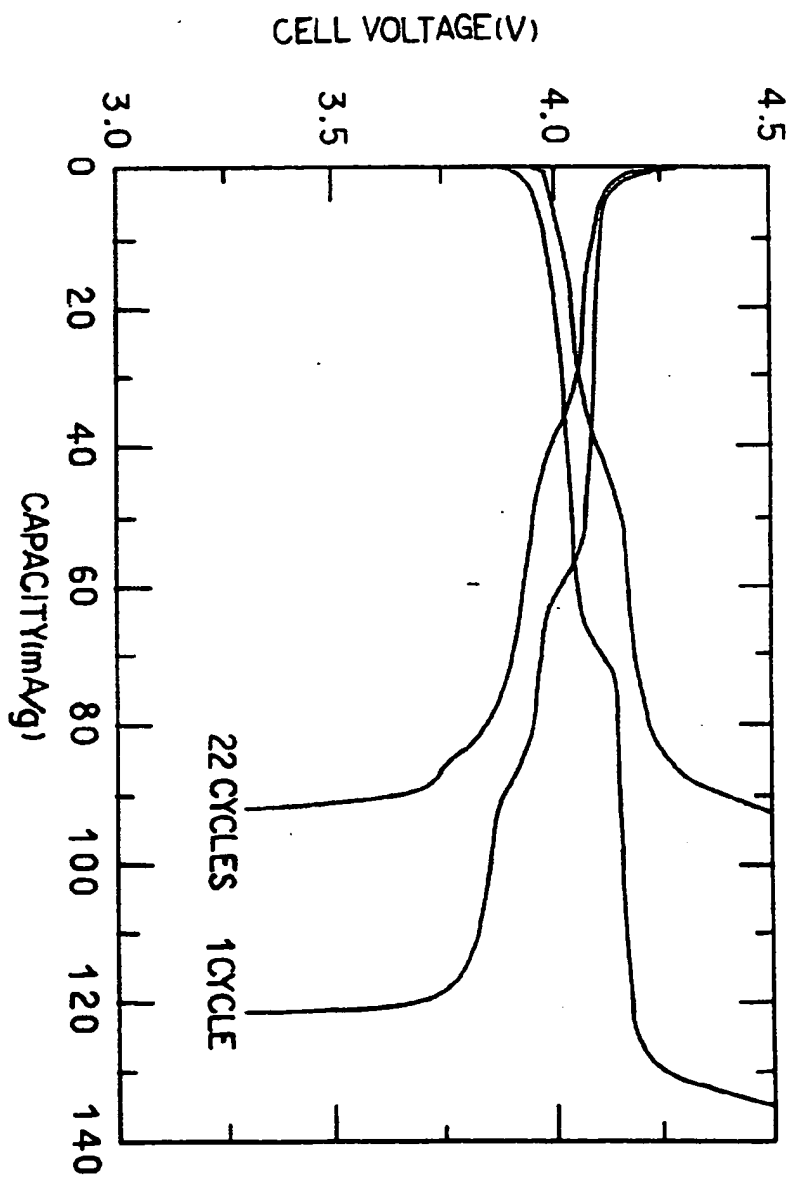
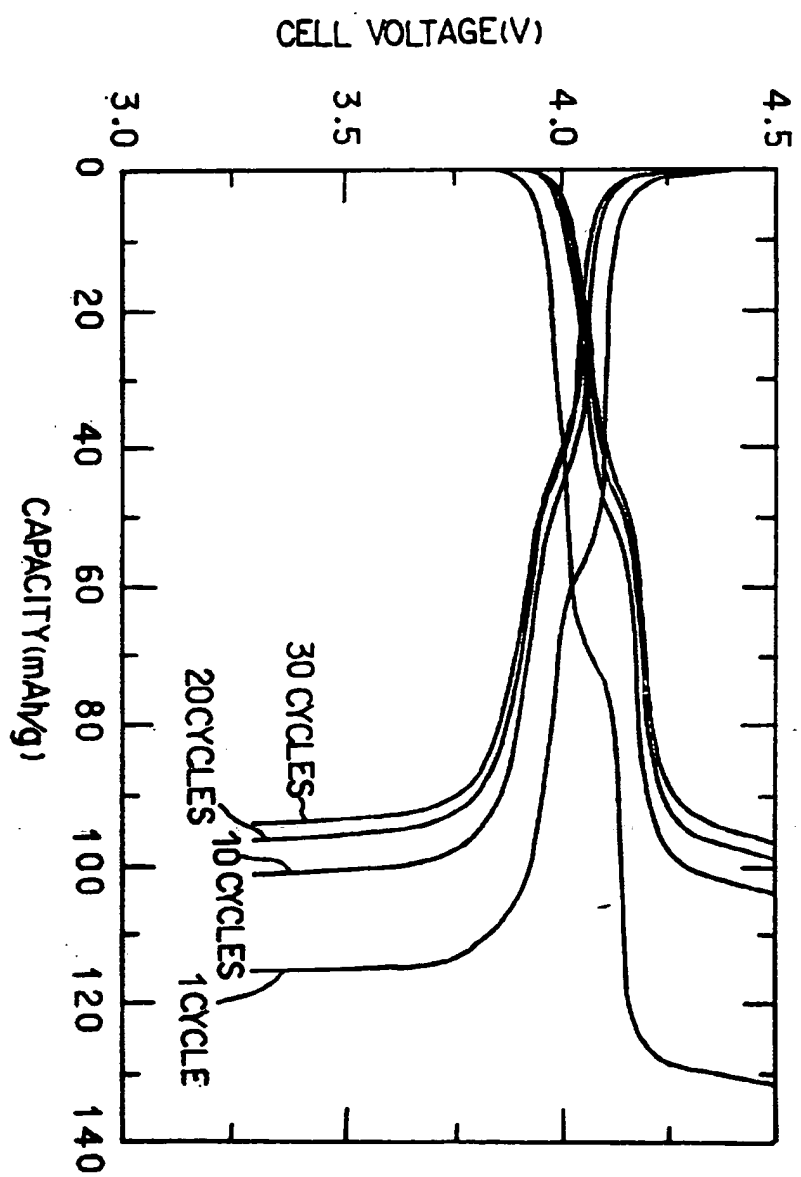


FIG. 5



**A LITHIUM MANGANESE OXIDE POWDER, PREPARATION METHOD THEREOF, AND A LITHIUM SECONDARY BATTERY ADOPTING A POSITIVE ELECTRODE CONTAINING THE SAME AS AN ACTIVE MATERIAL**

The present invention relates to a lithium (Li) secondary battery, and more particularly,  
5 lithium manganese oxide in a fine powder form, a preparation method thereof, and a Li secondary battery adopting a positive electrode containing the lithium manganese oxide as an active material.

In a Li secondary battery, the charging/discharging capacity of an active material depends on the particle size of the active material and the particle structure. That is, as the  
10 particle size of the active material is smaller, the diffusion rate of Li ions increases, thereby increasing the charging/discharging capacity of a positive electrode. Also, in the case the particle structure facilitates diffusion of Li ions, the charging/discharging capacity of the positive electrode increases.

Lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ) has been used as a positive electrode active material  
15 in a Li secondary battery, like lithium nickel oxide ( $\text{LiNiO}_2$ ) and lithium cobalt oxide ( $\text{LiCoO}_2$ ). In particular, lithium manganese oxide has been preferred because lithium manganese oxide provides a high energy density at low costs without causing pollution.

There are various methods for preparing such positive electrode active material: two of them are as follows.

20 First, according to a solid solution synthesis method, lithium manganese oxide can be obtained by mixing lithium salt and manganese oxide using a ball mill and then heating.



the mixture. During the thermal process, lithium salt is decomposed and decomposed lithium ions are incorporated into the lattice structure of manganese oxide, thereby resulting in lithium manganese oxide. Here, as the thermal process temperature and time increase, the particle size increases. Thus, it is important to appropriately control the temperature and time of the thermal process.

As another method, there is a sol-gel method which has been widely used for ceramic synthesis. Because the sol-gel method can synthesis oxides having a comparatively stable structure, the method has been used to prepare lithium metal oxide which is used as a positive electrode active material of the Li secondary battery. According to the sol-gel method, a sol-state solution containing raw material and a chelate compound is prepared, and then Li and metal cation are combined with the chelate compound under appropriate conditions. Then, the chelate is decomposed and then removed through a thermal process, thereby resulting in lithium metal oxide having a stable structure. The sol-gel method results in a lithium metal oxide powder, which is finer than that obtained by the above solid solution synthesis method. However, additives (particularly, chelate compound) are expensive, and the overall process is also complicated because hydrolysis-condensation, and flocculation must be repeated.

According to a first aspect of the present invention, there is provided a lithium manganese oxide ( $\text{Li}_x\text{Mn}_2\text{O}_4$ , where  $x$  is 1 ~ 1.05), in which the lithium manganese oxide is in a fine powder form and the particle of the powder has an octahedron shape.

Preferably, the size of the particle is  $0.3 \sim 1 \mu\text{m}$ , and a specific surface area thereof is  $3 \sim 4.5 \text{ m}^2/\text{g}$ .

According to a second aspect of the present invention, there is provided a method of preparing a fine lithium manganese oxide ( $\text{Li}_x\text{Mn}_2\text{O}_4$ , where  $x$  is  $1 \sim 1.05$ ) powder, comprising the steps of: (a) dissolving lithium acetate and manganese acetate in a solvent; (b) adding gelatin in the solution obtained in the step (a), and removing the solvent to form a gel; (c) forming a lithium manganese oxide powder by calcinating the gel at  $300 \sim 500^\circ\text{C}$ ; (d) grinding the powder and sintering the ground product at  $750 \sim 850^\circ\text{C}$  for  $6 \sim 12$  hours; and (e) cooling the sintered product.

Preferably, the particle of the fine lithium manganese oxide powder has an octahedron shape, the size of the particle is  $0.3 \sim 1\mu\text{M}$ , and the specific surface area thereof is  $3 \sim 4.5\text{m}^2/\text{g}$ .

According to a third aspect of the present invention, there is provided a lithium secondary battery including a positive electrode using a lithium metal oxide as a positive electrode active material, a carbonic negative electrode and a hydrophobic electrolyte, wherein the lithium metal oxide of the positive electrode is lithium manganese oxide ( $\text{Li}_x\text{Mn}_2\text{O}_4$ , where  $x$  is  $1 \sim 1.05$ ) having octahedron particle shape.

Examples of the present invention will now be described in detail with reference to the accompanying drawings, in which:

FIG. 1 is a graph showing changes in the capacity of active material according to the repeated chargings and dischargings, in a lithium (Li) secondary battery containing lithium manganese oxide sintered at  $800^\circ\text{C}$  for 6 hours, according to a first example of the present invention (at a charging/discharging rate of  $0.3\text{C}$ );

FIG. 2 is a graph illustrating a high-rate charging/discharging characteristic (1C) of the Li secondary battery containing the lithium manganese oxide sintered at 800°C for 6 hours, according to the first example of the present invention;

FIG. 3 is a scanning electron microscopic photograph of a lithium manganese oxide according to a third example of the present invention;

FIG. 4 is a graph illustrating changes in the capacity of active material according to repeated chargings and dischargings, in the lithium (Li) secondary battery containing lithium manganese oxide according to the third example of the present invention (at a charging/discharging rate of 0.3C); and,

FIG. 5 is a graph illustrating changes in the capacity of active material according to repeated chargings and dischargings, in a lithium (Li) secondary battery containing lithium manganese oxide according to a fourth example of the present invention.

In the present invention, gelatin is used in a process of preparing a lithium manganese oxide powder. Gelatin, a protein, has an amino group and a carbonyl group. These functional groups act as reactive sites for chelating cations. In the case of gelatin, the number of reactive sites per molecule is approximately 550 times that of citrate used as a chelate in a conventional sol-gel method. Thus, the reactivity of gelatin is very high, thereby lowering preparation costs of the positive electrode active material. When using gelatin in order to prepare the positive electrode active material by the sol-gel method, the gelatin chelates Li, as the major component of the positive electrode active material, with manganese cation, thereby stabilizing the structure of the resultant lithium manganese oxide. Because a small amount of gelatin can change inorganic cations into a gel in a frozen state, the conventional problem related to the complicated process including flocculation or hydrolysis-condensation is minimized, thereby reducing the time required for the overall synthesis process. The

structure determined by the gelatin is maintained after the gelatin is removed through the following calcination and sintering processes, so that most lithium manganese oxide particles have an octahedron shape, thereby increasing a specific surface area.

A method of preparing lithium manganese oxide according to the present invention will be described in detail. After dissolving lithium acetate and manganese acetate in a solvent, gelatin is added to the solution. Here, lithium acetate and lithium manganese are mixed with a mole ratio of 1:2 ~ 1.05:2, which is similar to a general ratio applied for lithium manganese oxide used as a positive electrode active material of the Li secondary battery. Preferably, the gelatin is added in amount of 5 ~ 15 Wt% based on the total amount of the lithium acetate and the lithium manganese. The effect of the present invention is not affected by the amount of gelatin. However, the above range of the gelatin provides an appropriate solubility. Also, alcohol or distilled water, preferably, methanol or ethanol, is used as the solvent.

Then, when completely dissolving the gelatin by increasing the temperature to 90 ~ 150°C, the solvent is spontaneously evaporated and removed during this process, resulting in a viscous material. By cooling the temperature to room temperature, a transparent gel is obtained. When calcinating the gel by increasing the temperature to 300 ~ 500°C, the gel is slowly solubilized at the initial stage, generating bubbles. Then, decomposition of polymer starts. During this process, carbon dioxide and vapor are generated, thereby resulting in lithium manganese oxide powders. After grinding the lithium manganese oxide powder, a sintering process is performed for 6 ~ 12 hours while the temperature is increased to approximately 750 ~ 850°C, preferably, 800°C, at a temperature increase rate of 1 ~ 3°C/minute. Here, the sintering for 6 hours or less at 800°C is not sufficient. On the contrary, sintering for 12 hours or more at 800°C causes growth of the particles, thereby reducing a specific surface area. Also, the reduced specific surface area reduces capacity.

Then, the resultant of the sintering process is cooled at a rate of  $0.1 \sim 2^{\circ}\text{C}/\text{minute}$ , resulting in fine lithium manganese oxide powder, the particle of which has an octahedron shape, as the positive electrode active material of the present invention. The octahedron shape of the fine particle of the lithium manganese oxide powder allows easy intercalation/deintercalation of the lithium ions, thereby increasing capacity of the battery.

A positive electrode can be formed from the positive electrode active material by a general method without restrictions in the method therefor. Also, when manufacturing a Li secondary battery using the formed positive electrode, a conductor and a bonding agent, which have been widely used, are used. Acetylene black or carbon black may be used as the conductor, and polyvinylidenefluoride may be used as the bonding agent.

Hereinafter, the present invention will be described in detail through the following examples. However, the present invention is not limited to the following examples.

#### Example 1

0.5M of lithium acetate ( $\text{CH}_3\text{CO}_2\text{Li}\cdot\text{H}_2\text{O}$ ) and 0.2M of manganese acetate ( $(\text{CH}_3\text{CO}_2)_2\text{Mn}\cdot 4\text{H}_2\text{O}$ ) were slowly added to 50ml of methanol and completely dissolved by stirring. Then, 4g of gelatin was added to the solution, and then the mixture was heated at  $120^{\circ}\text{C}$  to remove the solvent, thereby forming a gel. The gel was calcinated at  $400^{\circ}\text{C}$  to form a lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ) powder. Then, the powder was ground with a mortar. The ground lithium manganese oxide was sintered by increasing the temperature to approximately  $800^{\circ}\text{C}$  at a rate of  $1^{\circ}\text{C}/\text{min}$  for 6 hours, and then cooled to room temperature at a rate of  $0.5^{\circ}\text{C}/\text{min}$ , resulting a fine powdered lithium manganese oxide. The specific surface area of the obtained lithium manganese oxide was  $4.5\text{m}^2/\text{g}$ .

6ml. of N-methylpyrrolidone was added to a mixture containing the obtained lithium manganese oxide powder, carbon black and polyvinylidenefluoride (88:5:7wt%) and then mixed until a paste was formed. After putting the paste in a vacuum oven to remove bubbles, the paste was coated on an aluminum foil to a thickness of  $200\mu\text{m}$  using a doctor blade. The coated resultant was dried in a  $150^{\circ}\text{C}$  vacuum oven for 2 hours and then pressed to form a polar plate. The polar plate was cut into a 2cm-diameter circle to form a positive electrode for a coin cell. Then, lithium foil was cut into the same size as the anode, and then compressed with a nickel foil, resulting in an anode. The obtained anode is welded into a glove box in the cap of the coin cell. Lastly, a separator (3M) and an electrolyte (EC/DMC (ethylenecarbonate/dimethylenecarbonate) +  $\text{LiPF}_6$ ) were incorporated, resulting in a coin cell.

The obtained coin cell was charged and discharged at a rate of 0.3C, and the result is shown in FIG. 1. As shown in FIG. 1, the initial capacity of the active material was 129mAh/g and the capacity of the active material after 30 charging/discharging cycles was nearly the same as that at 20 charging/discharging cycles.

Also, the change in capacity of the active material was measured after charging and discharging the coin cell at a high rate (1C) up to 100 cycles, and the result is shown in FIG.

2.

As is evident from FIG. 2, the capacity of the active material has rather slightly increased after 80 chargings and dischargings. Also, the capacity of the active material after 100 chargings and dischargings at a high rate reaches 75% of the initial capacity of the active material. From the above result, it is obvious that a good cell having a high-rate charging/

discharging characteristic can be obtained if the lithium manganese oxide of the present invention is used as a positive electrode active material of the lithium secondary battery.

### Example 2

4g of gelatin was completely dissolved in 50ml of distilled water. Then, 1M of lithium acetate ( $\text{CH}_3\text{CO}_2\text{Li}\cdot 2\text{H}_2\text{O}$ ) and 2M of manganese acetate ( $(\text{CH}_3\text{CO}_2)_2\text{Mn}\cdot 4\text{H}_2\text{O}$ ) were added to the solution and completely dissolved by stirring. Then, the resultant solution was heated to  $90^\circ\text{C}$  to remove the solvent, thereby forming a gel. Other than the above, a fine powdered lithium manganese oxide ( $\text{LiMn}_2\text{O}_4$ ) in a fine powder form and a lithium coin cell using the lithium manganese oxide as a positive electrode active material were fabricated by the same method as Example 1.

The charging/discharging test was performed on the obtained lithium coin cell. As a result, the capacity characteristic of the active material and a high-rate charging/discharging characteristic was good as in the result of Example 1.

### Example 3

A fine powdered lithium manganese oxide was prepared by the same method as Example 1, except that the ground lithium manganese oxide was sintered at  $800^\circ\text{C}$  for 12 hours. The specific surface area of the fine lithium manganese oxide powder was  $3.7\text{m}^2/\text{g}$ . A photograph of the fine powder, taken by a scanning electron microscope (SEM), is shown in FIG. 3. As shown in FIG. 3, the fine powder has a octahedron shape, and the particle size is less than  $1\mu\text{m}$  or less.

A coin cell was fabricated using the lithium manganese oxide as a positive electrode active material by the same method as Example 1. Also, the charging/discharging test was performed on the coin cell, and the result is shown in FIG. 4.

As shown in FIG. 4, the initial capacity of the active material was 123mAh/g, which is still above a preferred capacity level. Also, the capacity of the active material was decreased as the charging/discharging cycle was repeated. However, such decrease in capacity of the active material was within an allowable range. It is believed that the reason why the initial capacity of the active material is decreased compared to Example 1 is because the specific surface area of the powder is decreased as the powders are grown with the increase of the sintering duration.

#### Example 4

A fine lithium manganese oxide ( $\text{Li}_{0.05}\text{Mn}_2\text{O}_4$ ) powder was prepared and a lithium coin cell was fabricated using the lithium manganese oxide powder as a positive electrode active material, by the same method as Example 3, except that lithium acetate and manganese oxide were added with a mole ratio of 1.05:2. A charging/discharging test was performed on the lithium coin cell, and the result is shown in FIG. 5.

As shown in FIG. 5, the initial capacity of the active material was 117mAh/g, and the capacity of the active material was scarcely decreased by repeating the charging/discharging cycles.

As described above, the fine powdered lithium manganese oxide powder of the present invention has an octahedron shape and can increase the capacity due to its fineness when



being used as a positive electrode active material for a lithium secondary battery. Also, the lithium manganese oxide can be easily prepared at low cost compared with the conventional case. Thus, the lithium secondary battery adopting a positive electrode containing the lithium manganese oxide as a positive electrode active material has an improved capacity characteristic and a high-rate charging/discharging characteristic, which expands the applicable range thereof.

**CLAIMS:**

1. A lithium manganese oxide ( $\text{Li}_x\text{Mn}_2\text{O}_4$ , where  $x$  is  $1 \sim 1.05$ ), in which the lithium manganese oxide is in a fine powder form and the particle of the powder has an octahedron shape.

5 2. A lithium manganese oxide according to claim 1, wherein the size of the particle is  $0.3 \sim 1\mu\text{M}$ , and a specific surface area thereof is  $3 \sim 4.5\text{m}^2/\text{g}$ .

3. A method of preparing a fine lithium manganese oxide ( $\text{Li}_x\text{Mn}_2\text{O}_4$ , where  $x$  is  $1 \sim 1.05$ ) powder, comprising the steps of:

(a) dissolving lithium acetate and manganese acetate in a solvent;

10 (b) adding gelatine in the solution obtained in the step (a), and removing the solvent to form a gel;

(c) forming a lithium manganese oxide powder by calcinating the gel at  $300 \sim 500^\circ\text{C}$ ;

(d) grinding the powder and sintering the ground product at  $750 \sim 850^\circ\text{C}$  for  $6 \sim 12$  hours; and,

15 (e) cooling the sintered product.

4. A method according to claim 3, wherein the particle of the fine lithium manganese oxide powder has an octahedron shape.

5. A method according to claim 3 or 4, wherein the size of the particle is  $0.3 \sim 1\mu\text{M}$ , and the specific surface area thereof is  $3 \sim 4.5\text{m}^2/\text{g}$ .

6. A method according to any of claims 3 to 5, wherein the solvent used in the step (a) is alcohol or distilled water.

7. The method of claim 3, wherein the content of the gelatine in the step (b) is 5 ~ 15Wt% based on the total weight of lithium acetate and manganese acetate.

5 8. A lithium secondary battery including a positive electrode using a lithium metal oxide as a positive electrode active material, a carbonic negative electrode and a hydrophobic electrolyte, wherein the lithium metal oxide of the positive electrode is lithium manganese oxide ( $\text{Li}_x\text{Mn}_2\text{O}_4$ , where x is 1 ~ 1.05) having octahedron particle shape.

9. A lithium secondary battery according to claim 8, wherein the size of the particle is  
10 0.3 ~ 1 $\mu\text{m}$ , and the specific surface area thereof is 3 ~ 4.5 $\text{m}^2/\text{g}$ .



Application N : GB 9818461.7  
Claims searched: 1-9

Examiner: Dr. Guy Standen  
Date of search: 5 November 1998

**Patents Act 1977**  
**Search Report under Section 17**

**Databases searched:**

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.P): C1A (AVG1, APB5)

Int Cl (Ed.6): C01D (15/00, 15/02), C01G (45/02, 45/12), H01M (4/50)

Other: ONLINE: WPI

**Documents considered to be relevant:**

Category	Identity of document and relevant passage	Relevant to claims
X	EP 0712173 A1 JAPAN STORAGE BATT CO LTD see whole document	1-7
X	EP 0413313 A2 SANYO ELECTRIC CO LTD see example D <sub>3</sub> and claim 1	1, 2, 8 and 9
X	WO 96/12676 VALENCE TECH INC see claims 1-4 and 19	1, 2, 8 and 9

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